# **Division of Materials Chemistry** - Inorganic Photonics Materials -

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(D Eng)



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University of Sassari, Italy, 17 January - 14 February 2005 Université Paris 6, France, 7 November 2005 Université Paris 6, France, 7 November 2005

## **Scope of Research**

In this laboratory, amorphous and polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, optical nonlinearity and photocatalysis are the target materials, which are synthesized by sol-gel, multi-cathode sputtering, melt-quenching and sintering methods and so on. Aiming at highly functional materials the structures are investigated by X-ray diffraction techniques, high-resoluction NMR, thermal analysis, various laser spectroscopies and ab initio molecular orbital calculations.

## **Research Activities (Year 2005)**

#### **Presentations**

Optical Characteristics of Organic-inorganic Hybrid Material Derived Through Non-hydrolytic Reaction and Photo-Polymerization, Kang E., Takahashi M., Yoko T., The 105th Annual Meeting the American Ceramics Society, Baltimore, 15 - 17 April.

Preparation and NLO Properties of Dye-doped Polysiloxane-based Glass Thick Films, Menaa B., Takahashi M., Mizuno M., Tokuda Y., Yoko T., MC7: Functional Materials for the 21st Century, Edinburgh (UK), 6 - 9 July.

Organic-inorganic Hybrid Materials Prepared through Non-aqueous Acid-base Reactions, Takahashi M., Mizuno M., Kakiuchida H., Menaa B., Tokuda Y., Yoko T., 13th International Workshop on Sol-gel Science and Technology (Sol-gel2005), Los Angels, USA, 21 - 26 September.

Optical Characteristics of Organic-inorganic Hybrid Material Derived through Non-hydrolytic Reaction and Photo-polymerization, Kang E., Takahashi M., Yoko T., 6th Pacificrim Conference on Ceramics and Glass Technology, Maui, Hawaii, USA, 16 September.

#### Grants

Yoko T., Preparation of Organic-inorganic Hybrid Lowmelting Glasses through Acid-base Reaction, Asahi Glass Foundation, 1 April 2004 - 31 March 2005.

Takahashi M., Inhomogeneous Structures in the Glasses, Grant-in-Aid for Scientific Research for Encouragement of Young Scientists (A), 1 April 2004 - 31 March 2006.

Takahashi M., Development of Photonics Materials Based on the Organic-inorganic Hybrid Low Melting Glasses, PRESTO, Japan Science and Technology Agency, 1 November 2002 - 31 March 2006.

Takahashi M., Organic-inorganic Hybrid Low-melting Glasses Doped with Optical Active Centers via Nonaqueous Acid-base Reaction, Murata Scientific Foundation, 1 July 2004 - 31 June 2005.

Takahashi M., Fabrication of Large Area Photonic Films, Toyota Physical & Chemical Research Institute, 1 April

#### **Fabrication of Periodic Photonic Structure** of TiO<sub>2</sub> and Other Oxides on Sol-gel Dip **Coated Films through Photo-Polymerization Induced Phase Separation (PIPS)**

By combining PIPS with sol-gel coating technique, we can obtain photonic structures shown in Fig. 1. Pictures show the TiO<sub>2</sub> phase grating obtained by holographic illumination of Ar+-ion laser light (inset shows the SEM image of the obtained gratings). The periodicity could be controlled in the range from 500 nm to 20 µm depending on the holographic condition of irradiated laser light. When the PIPS and sol-gel conditions are appropriately controlled, we can fabricate periodic structure without laser (coherent) light source. Fig. 2 shows an AFM image of the TiO<sub>2</sub> 2D-photonic structure obtained by the present method using a black light as UV source. The 2D structure is self-organized on the substrate. This method has a great advantage compared to the photo-polymerization method of vinyl-modified metal alkoxides system. With complete condensation, a large value of  $\Delta n$  is expected.

### Structural Study on Organically-Modified **Polysiloxane Glasses**

We have already reported that low-melting glass can be prepared using a gel derived by the sol-gel method. The glasses with compositions of xPh2SiO2/2-(1-x)PhSiO3/2 (0  $< x \le 30$ ) were prepared and their softening temperatures are widely dispersed around 150°C. In order to examine factors affecting the softening behavior, structural study has been performed using <sup>29</sup>Si MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectroscopy and GPC (Gel Permeation Chromatography) measurements. First, we obtained the frequency at G" (the imaginary part of the elastic modulus) =  $10^3$  Pa using viscoelastic measurements. Second, we acquired the condensation degree of Si, <m>, which is the number of Si-O-Si bonding per one Si by NMR spectra and the molecular volume, <M>, by GPC measurements. Finally, we have found a relation between the frequency at G"=10<sup>3</sup> Pa, the condensationdegree and molecular volume as follows,

 $\log_{G''=10^{3}Pa} = -9.2 < m > -5.0 \log < M > + const.$ 

We have also found that the rate of increase in elastic modulus induced by heat-treatment decreases with increasing amount of Ph2SiO2/2 unit.



of the obtained grating. Figure 2. 2D photonic structure of TiO2 obtained by irradiating a black light. The periodic structure was obtained 10µm by controlling PIPS conditions

SEM imag

1*µ* n

10 µ m

Figure 1. Titania phase grat-

ing obtained by PIPS in com-

bination with the sol-gel coat-

ing technique. Inset shows the

SEM image of fractured edge

2005 - 31 March 2006.

Kakiuchida H., Softening Behavior of Organic-inorganic Hybrid Glasses and its Application for Photonic Devices, ICR Grants for Young Scientists.

#### Awards

6th Pacificrim Conference on Ceramics and Glass Technology, Student Poster Award, "Fabrication of TiO2 Periodic Structure by the Photopolymerization-induced Phase Separation Method", Maeda T., Takahashi M., Yao J.,

Tokuda Y., Nishii J. and Yoko T., 6th Pacific Rim Conference on Ceramic and Glass Technology, 11 - 16 September 2005.

BCSJ Paper Award, "Conducting and Magnetic Properties of 1-Ethyl-3-methylimidazolium (EMI) Salts Containing Paramagnetic Irons: Liquids [EMI][M<sup>III</sup>Cl<sub>4</sub>] (M = Fe and Fe<sub>0.5</sub>Ga<sub>0.5</sub>) and Solid [EMI]<sub>2</sub>[Fe<sup>II</sup>Cl<sub>4</sub>]", Yoshida Y., Otsuka A., Saito G., Natsume S., Nishibori E., Takata M., Sakata M., Takahashi M., and Yoko T.